



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number: 0 483 184 B1

⑫

EUROPEAN PATENT SPECIFICATION

⑮ Date of publication of patent specification :
26.01.94 Bulletin 94/04

⑯ Int. Cl.⁵: C22C 1/08

⑰ Application number : 90910522.3

⑲ Date of filing : 11.07.90

⑳ International application number :
PCT/NO90/00115

㉑ International publication number :
WO 91/01387 07.02.91 Gazette 91/04

㉒ A PROCESS OF MANUFACTURING PARTICLE REINFORCED METAL FOAM AND PRODUCT THEREOF.

The file contains technical information submitted after the application was filed and not included in this specification

㉓ Priority : 17.07.89 NO 892925

㉔ Proprietor : NORSK HYDRO A.S.
N-0240 Oslo 2 (NO)

㉔ Date of publication of application :
06.05.92 Bulletin 92/19

㉕ Inventor : RUCH, Wolfgang, Walter
Munkparken 18
DK-6240 Logumkloster (DK)
Inventor : KIRKEVAG, Bjorn
Borsetlauvet 16
N-6620 Alvundeid (NO)

㉔ Publication of the grant of the patent :
26.01.94 Bulletin 94/04

㉖ Representative : Huber, Bernhard, Dipl.-Chem.
Patentanwälte H. Weickmann, Dr. K. Fincke
F.A. Weickmann, B. Huber Dr. H. Liska, Dr. J.
Prechtel, Dr. B. Böhm Postfach 86 08 20
D-81635 München (DE)

㉔ Designated Contracting States :
AT BE CH DE DK ES FR GB IT LI LU NL SE

EP 0 483 184 B1

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

The present invention relates to a process of providing metal foam and more particularly to a process resulting in provision of thin wall closed cell particle reinforced metal foam.

5 Foamed metals, as well as foamed ceramics and plastics, due to their unique combination of properties and light weight are earning growing attention as engineering materials.

There are several ways to produce foams. Different foaming techniques are known such as incorporating hydrides in the molten metal or adding organic compounds which release gases on heating. Vapor deposition on polymeric substrates or casting of metal around granules which are then leached out leaving a porous metal 10 structure are other examples of providing metals with cellular structure.

The process of foam formation using blowing agents is affected by the surface tension and viscosity of the actual melt. The viscosity counteracts bursting of the cell walls during a progressive increase in the volume of the formed bubbles, while a low surface tension will favour formation of thin bubble walls.

15 The properties of foams being gas-in-solid dispersions are largely determined by their density, but the cell size, structure and their distribution are also important parameters influencing the properties.

In general such foamed metals are produced by adding a gas evolving compound to the molten metal followed by heating of the resultant mixture to decompose the compound and to produce expanding cellulating gases. The foaming compound is usually metal hydride such as TiH_2 or ZrH_2 , and after the foaming step the mould is cooled to form a solid foam material. Cells of non-uniform structure and/or undesirably large size are 20 experienced due to the difficulties with uniform distribution of the evolving gas through the whole volume of the foamed metal.

25 GB patent No. 1.287.994 discloses a process for preparation of metal foams applying a viscosity increasing agent comprising an inert gas or an oxygen containing material gaseous at the melt conditions and treating the thus produced viscous melt with a foaming agent. Air, nitrogen, carbon dioxide, argon and water are preferably used in the process as viscosity increasing agents in amounts from 1 to 6 grams per 100 grams of metal alloy. Metal hydrides are used as foaming agents (hafnium, titanium or zirconium hydrides) in amounts of from 0,5 to 1,0 grams per 100 grams of alloy.

30 Preferably the increase in viscosity is enhanced by the presence of a promoter metal, e.g. from 4 to 7 weight% magnesium is used in aluminium alloys. A good mixing technique is required, the addition of foaming agents is usually carried out at a temperature lower than addition of the viscosity increasing agent in a separate second vessel. The disclosed batchwise process, achieving better foams with regard to uniform size and distribution of the cells, and claiming a certain reduction in the consumption of foaming agents, is a rather complicated time consuming and expensive process requiring several process steps and units based on use of expensive heat decomposable gas evolving compounds (hydrides).

35 European patent application No. 0 210 803 discloses a similar batchwise method of producing foamed metals based on use of from 0,2 to 8,0 weight% metallic calcium as viscosity adjusting agent and titanium hydride in amounts of from 1 to 3 weight% of the molten melt as foaming agent.

40 Still another method of producing cellularized metal by decomposition of a heat-decomposable gas evolving compound in molten metal is disclosed in US patent No. 3.297.431. The improvement comprises addition of an intimately dispersed, finely divided powder to the metal prior to decomposition of the gas evolving compound (carbonates or hydrides), or dissolving of gas in the melt. The stabilizing powders may be metals or non-metals, elements or compounds, and two wettable powders are preferentially used where one of which forms a solid alloy with the metal. Usually the gas is dissolved at one pressure and then evolved at a second lower pressure.

45 A drawback in common for the hitherto known processes is that all of them are batchwise operating processes using either expensive gas evolving compounds or dissolved gases as cellulating means and viscosity increasing or stabilizing additives to achieve quality metal foams.

50 Furthermore, the prior art processes require a close control with the temperature and pressure conditions at different steps of the process. Consequently, so far there is no method operating on an industrial scale in an economical way offering a low cost metal foam to compete with other engineering materials.

Accordingly, it is an object of this invention to provide a simple low cost method for preparation of quality foams.

Another object of the invention is to provide a method for upgrading of scrap metal material.

55 Still another object of the invention is to provide a novel type of particle reinforced metal foam having improved mechanical properties.

The process of manufacturing a particle reinforced metal foam in accordance with the invention is defined in the accompanying claims.

The invention in its various aspects will be described in details, and various other objects, advantages and

additional features thereof will become more apparent from the following description which is to be read in conjunction with the attached drawings, Fig. 1-4, where

Fig. 1 shows schematically in the form of a flow-sheet the process of preparation of metal foam according to the invention,

Fig. 2 displays a natural size contact print of the foamed metal sample prepared according to the invention,

Fig. 3 shows an optical metalograph picture of the closed cell Al-foam structure,

Fig. 4 illustrates graphically results from a compression test conducted on foam samples.

Referring to Fig. 1, illustrating schematically the process of metal foam preparation, it has been found that a metal foam of the closed cell type structure having a uniform density and cell structure can be provided simply by feeding of finely dispersed cellulating gas into a molten particle reinforced metal matrix composite material (PMMC). No special additives adjusting the viscosity of the melt or particular precautions with regard to the distribution of the cellulating gas bubbles through the melt were required. The gas bubbles rise to the top of the melt and form foam gradually increasing in volume. No tendency to bursting of the foam cells when they reach the melt surface was observed. This indicates a (highly) stabilized surface of the gas bubbles. The upper portion of the foam cake solidifies and can be easily removed. Even foam which is not completely solidified can be removed without changing the cell structure due to the thick consistency of the formed foam. This is a quite important feature of the method according to the present invention, which allows to run the process continuously by transfer of semi-solidified foam to the moulds. There is even a possibility of subjecting the foam at this stage to certain forming operations, something which offers a flexibility with regard to the final shape of the resultant metal foam semiproducts.

Example 1

25 30 kg of an eutectic aluminium alloy (Si2Mg1Ni2,5) was melted in an open crucible. The molten alloy kept at a temperature of 650°C was added silicon carbide particles of an average size of 12 µm, and simultaneously CO₂ gas was finely dispersed through the melt by means of a special treatment rotor as disclosed in US patent No. 4.618.427. During the feeding of a CO₂ surplus into the formed molten composite material bubbles started to rise to the top of the melt forming a raising foam layer. The upper portions of the foam solidified with no sign of surface burst.

Fig. 2 shows in natural size a photographic picture of the resultant foam sample removed as the solidified top part of the foam cake. The cross-section of the sample exhibits a uniform distribution of cells having a diameter in the range of from 1 to 5 mm. The density of the sample was measured to 0,2 g/cm³.

Example 2

25 30 kg of scrap PMMC material (Al₂O₃ reinforced Al-alloy) was remelted in an open crucible. Pressurized air was applied as source of cellulating gas in this case, finely dispersed and distributed as described in Example 1.

40 Also in this case the resulting bubbles gave rise to a foamed structure when they reached the top of the melt in the crucible and were allowed to cool.

45 The achieved pores (cells) are essentially spherical and closed providing the foamed metal with isotropic properties in all directions, especially with regard to energy adsorption. Metallographic examination of the structure on the samples achieved from Example 1 reveals an extremely thin walled foam structure, as illustrated in Fig. 3. The wall thickness in this metallograph picture, magnification of 20, is in order of the reinforcing SiC particle size approximately 12 µm.

50 The mechanical behaviour of the produced foam is represented in Fig. 4 illustrating the results from the testing of compressive stress conducted on the samples from Example 1. The achieved flat stress/strain curve from the samples having an initial height of 26 mm applying a crosshead velocity of 2 mm/min. is typical for this type of material as long as the cell structure did not collapse completely. The energy absorption of this foam was determined to be 2 kJ/l foam, which is a very favourable value compared to the values reported in literature for commercially provided Al-foams. Obviously, the achieved improved mechanical properties of the resultant foams are a result of a beneficial influence from the reinforcing particles incorporated in the cell walls.

55 Evidently, the above described novel method of preparation of foamed metals according to the present invention offers several advantages both with regard to the economics of the process and the characteristics of the resulting foams.

First of all there is an opportunity to run the process continuously by continuous remelting or feeding of molten article reinforced metal material using a variety of available gases as a cellulating gas, e.g. N₂, Ar, CO₂, He and even pressurized air, which is normally easily available at low costs.

5 There are no special requirements to temperatures, pressure or uniform distribution of gas bubbles during the foaming and solidification of the resultant foamed metal. The density and to a certain extent also the cell size are simply controlled by dispersion of the cellulating gas through the melt, preferentially by applying the above special treatment rotor, but also other means ensuring finely dispersed bubbles can be applied. The foam accumulated on the top of the melt can be directly fed into moulds for solidification in desired shapes and dimensions or subjected to a certain grade of deformation/reshaping of the semisolidified foam.

10 Furthermore, even if it is possible to prepare the molten particle reinforced alloy in a separate process step using an active gas and addition of reinforcing particles prior to applying of the cellulating gas, the biggest potential of the present invention is an up-grading of low grade composite scrap material. This constantly increasing volume of composite scrap today represents a considerable problem since it can not simply be remelted or incorporated to the recycled secondary aluminium.

15 **Claims**

1. A process of manufacturing a particle reinforced metal foam in which a molten composite material comprising a metal matrix and finely divided reinforcing particles is continuously foamed by feeding cellulating gas into the melt thereby accumulating foamed composite metal material on the molten material surface, removing and solidifying the accumulated foam.
2. The process according to claim 1,
characterized in that
the molten composite material is provided by remelting of particle metal matrix composite material.
- 25 3. The process according to claim 1,
characterized in that
the composite material is formed in situ in the vessel by adding and distribution of reinforcing particles into the molten metal or alloy by means of an active gas.
- 30 4. The process according to claim 3,
characterized in that
the active gas is CO_2 gas and the particles are refractory particles.
- 35 5. The process according to one or more of the preceding claims,
characterized in that
the molten composite material is aluminium or aluminium alloy comprising refractory particles.
- 40 6. The process according to claim 1,
characterized in that
the cellulating gas is air.
7. Process according to one or more of the preceding claims,
characterized in that
the matrix metal is aluminium alloy reinforced by SiC particles.
- 45 8. Process according to claim 7,
characterized in that
the built foam exhibits a compressive strength of 0,2 kg/mm² at a density of 0,2 g/cm³.

50 **Patentansprüche**

1. Verfahren zum Herstellen eines partikelverstärkten Metallschaums, worin ein geschmolzenes Verbundstoffmaterial, das eine Metallmatrix und feinzerteilte Verstärkungspartikel umfaßt, kontinuierlich geschäumt wird, indem zellbildendes Gas in die Schmelze eingebracht wird, wobei geschäumtes Metallverbundstoffmaterial auf der Oberfläche des geschmolzenen Materials angesammelt wird und der angesammelte Schaum entfernt und verfestigt wird.
2. Verfahren nach Anspruch 1,

dadurch gekennzeichnet,
daß das geschmolzene Verbundstoffmaterial durch Wiedereinschmelzen von Partikel-Metallmatrix-Verbundstoffmaterial bereitgestellt wird.

5 3. Verfahren nach Anspruch 1,
 dadurch gekennzeichnet,
 daß das Verbundstoffmaterial im Behälter in situ durch Zugeben zu und Verteilen von verstärkenden Partikeln in dem geschmolzenen Metall oder der geschmolzenen Legierung mittels eines aktiven Gases gebildet wird.

10 4. Verfahren nach Anspruch 3,
 dadurch gekennzeichnet,
 daß das aktive Gas CO₂-Gas ist und die Partikel hitzebeständige Partikel sind.

15 5. Verfahren nach einem oder mehreren der vorhergehenden Ansprüche,
 dadurch gekennzeichnet,
 daß das geschmolzene Verbundstoffmaterial Aluminium oder Aluminiumlegierung ist, umfassend hitzebeständige Partikel.

20 6. Verfahren nach Anspruch 1,
 dadurch gekennzeichnet,
 daß das zellbildende Gas Luft ist.

25 7. Verfahren nach einem oder mehreren der vorhergehenden Ansprüche,
 dadurch gekennzeichnet,
 daß das Matrixmetall durch SiC-Partikel verstärkte Aluminiumlegierung ist.

30 8. Verfahren nach Anspruch 7,
 dadurch gekennzeichnet,
 daß der gebildete Schaum eine Druckfestigkeit von 0,2 kg/mm² bei einer Dichte von 0,2 g/cm³ aufweist.

Revendications

35 1. Procédé de fabrication d'une mousse métallique armée de particules, dans lequel une matière composite fondu, comprenant une phase métallique continue et des particules d'armature finement divisées, est mise sous forme d'une mousse continue par introduction d'un gaz de formation de cellules dans la matière fondu, avec accumulation de cette manière de la matière métallique composite en mousse à la surface de la matière fondu, puis par extraction et solidification de la mousse accumulée.

40 2. Procédé selon la revendication 1, caractérisé en ce que la matière composite fondu est formée par refusion de matière composite à phase continue métallique contenant des particules.

45 3. Procédé selon la revendication 1, caractérisé en ce que la matière composite est formée in situ dans un réservoir par addition et distribution de particules d'armature dans l'alliage ou métal fondu, à l'aide d'un gaz actif.

50 4. Procédé selon la revendication 3, caractérisé en ce que le gaz actif est CO₂ gazeux, et les particules sont des particules réfractaires.

55 5. Procédé selon une ou plusieurs des revendications précédentes, caractérisé en ce que la matière composite fondu est l'aluminium ou un alliage d'aluminium contenant des particules réfractaires.

60 6. Procédé selon la revendication 1, caractérisé en ce que le gaz de formation de cellules est l'air.

65 7. Procédé selon une ou plusieurs des revendications précédentes, caractérisé en ce que le métal de la phase continue est un alliage d'aluminium armé par des particules de SiC.

70 8. Procédé selon la revendication 7, caractérisé en ce que la mousse formée a une résistance à la compression de 2.10⁶ Pa (0,2 kg/mm²) pour une masse volumique de 0,2 g/cm³.

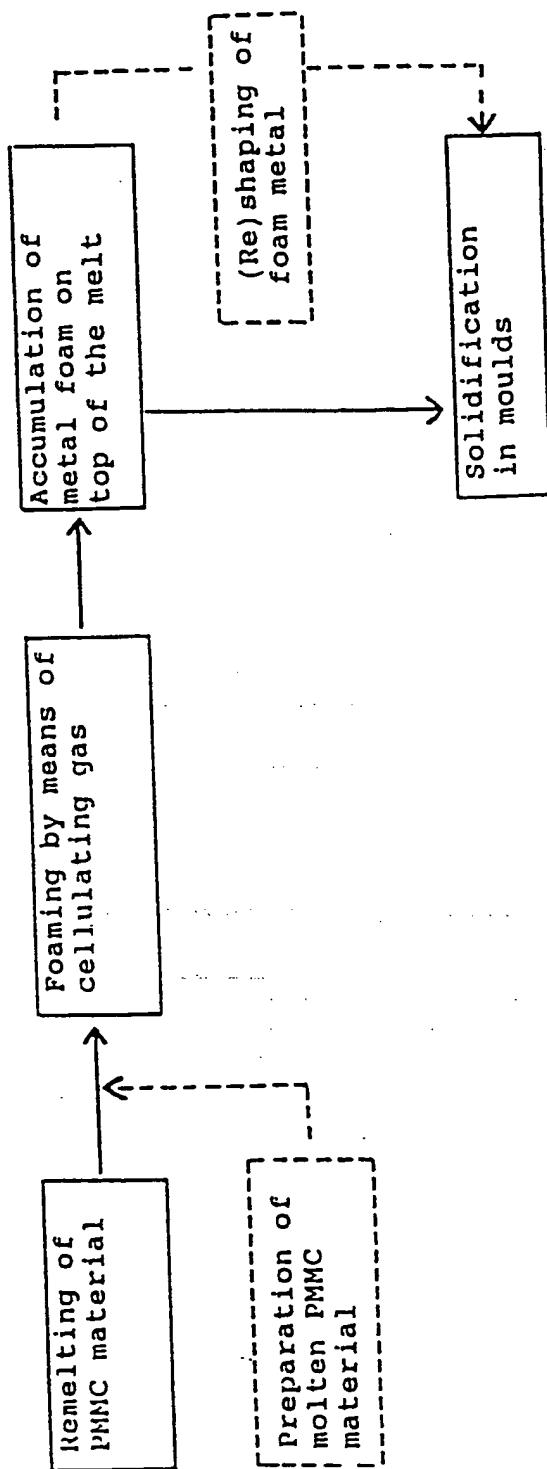


FIG. 1

BEST AVAILABLE COPY

EP 0 483 184 B1

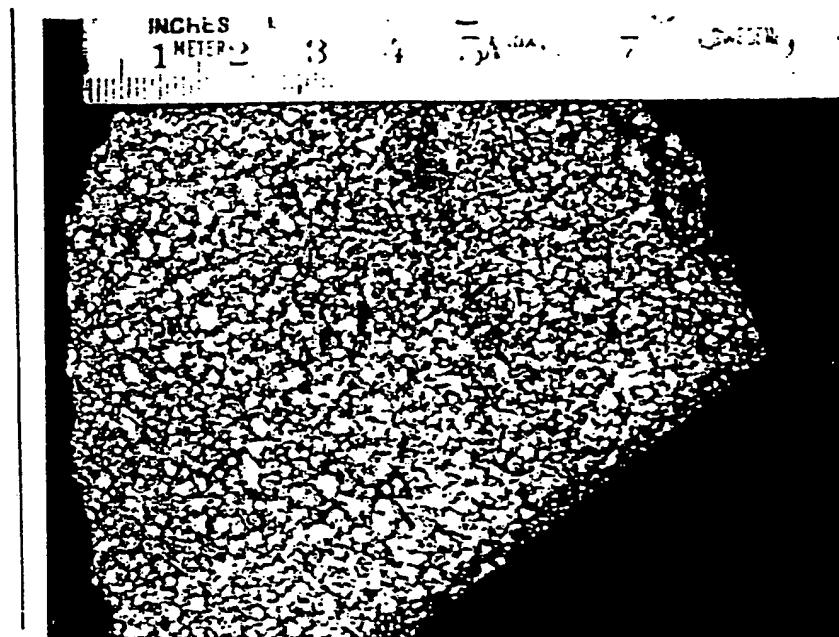


FIG. 2

BEST AVAILABLE COPY

EP 0 483 184 B1

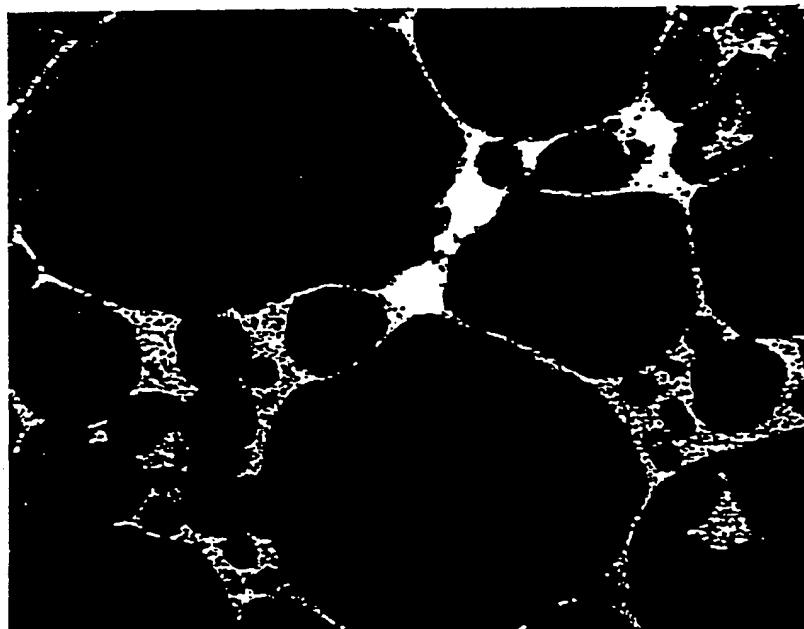


FIG. 3

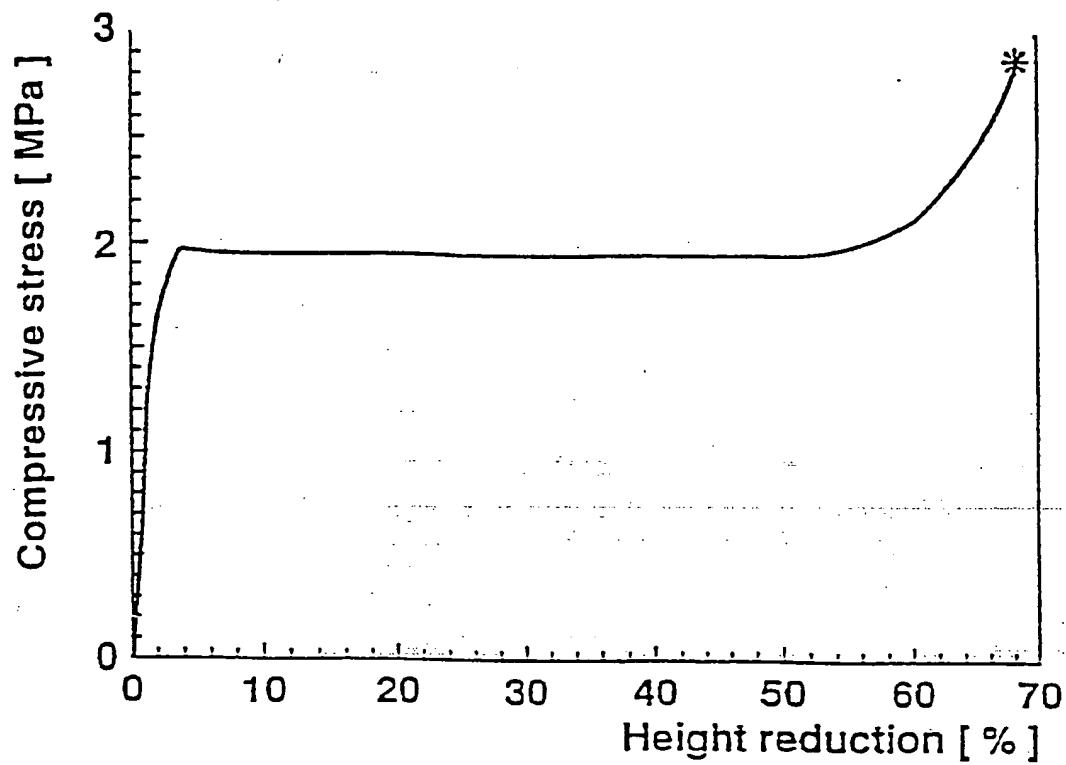


FIG. 4